

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-174626

(43)Date of publication of application : 29.06.2001

(51)Int. CI.

G02B 5/22

C08J 5/18

C08K 5/16

C08K 5/56

C08L 67/02

C09K 3/00

// C09B 57/10

(21)Application number : 11-354717

(71)Applicant : BRIDGESTONE CORP

(22)Date of filing : 14.12.1999

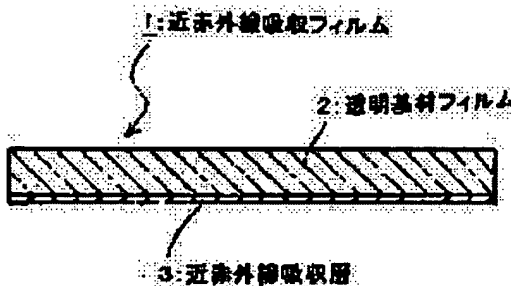
(72)Inventor : KOBAYASHI TAICHI  
SUGIMACHI MASATO  
SAITO SHINJI  
KITANO TETSUO  
KOTSUBO HIDESHI

## (54) NEAR INFRARED RAY ABSORPTION FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a high durability near infrared ray absorption film having excellent heat, humidity and ultraviolet rays resistance and suitable for the near infrared ray absorption film to be arranged on the front surface of a PDP(plasma display panel).

SOLUTION: The near infrared ray absorption film 1 comprises a near infrared ray absorption layer 3 formed on a surface of a transparent substrate film 2. A near infrared ray absorbing agent composed of a diimmonium compound and a specified copper type antioxidant such as a 1,2-benzenethiol copper complex compound are contained in the near infrared ray absorption layer 3.



---

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

**\* NOTICES \***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

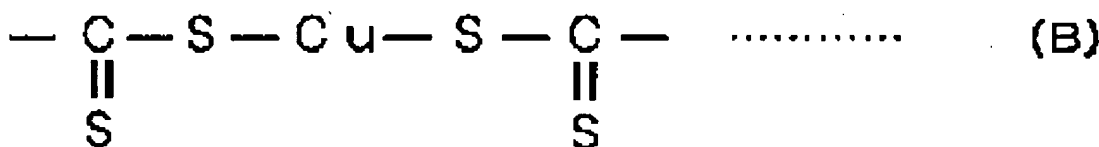
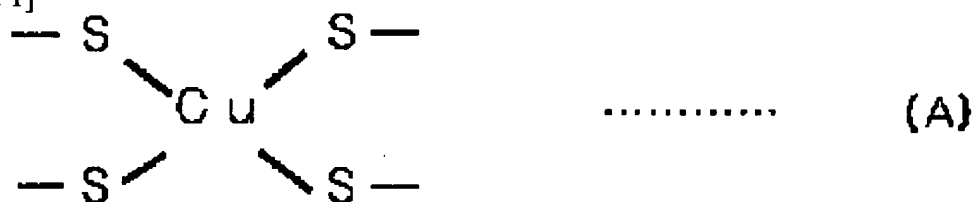
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

**CLAIMS**

[Claim(s)]

[Claim 1] The near infrared ray absorption film characterized by the near infrared ray absorbent which becomes this near infrared ray absorption layer from a G MONIUMU system compound, and the copper compound which has the copper complex and/or the following structure (B) of having the following structure (A) containing in the near infrared ray absorption film with which it comes to form a near infrared ray absorption layer in the front face of a transparence base material film.

[Formula 1]



[Claim 2] It is the near infrared ray absorption film characterized by being the layer which this near infrared ray absorption layer made distribute this G MONIUMU system compound, and this copper complex and/or a copper compound in a base polymer in claim 1.

[Claim 3] The near infrared ray absorption film with which the content rate of the G MONIUMU system compound in a near infrared ray absorption layer is characterized by being the 0.01 - 100 weight section to the base polymer 100 weight section in claim 2.

[Claim 4] The near infrared ray absorption film with which the copper complex in a near infrared ray absorption layer and/or the content rate of a copper compound are characterized by being the 0.01 - 100 weight section to the G MONIUMU system compound 100 weight section in claim 1 thru/or any 1 term of 3.

[Claim 5] The near infrared ray absorption film characterized by a base polymer being acrylic resin or polyester resin in claim 2 thru/or any 1 term of 4.

[Claim 6] The near infrared ray absorption film characterized by a transparency base material film being polyester film in claim 1 thru/or any 1 term of 5.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a near infrared ray absorption film, especially, is excellent in heatproof and moisture-proof \*\* ultraviolet resistance etc., and relates to a high endurance near infrared ray absorption film suitable as the near infrared ray absorption film arranged in the front face of a plasma display (PDP), and a heat ray absorption film stuck on the window glass of an automobile.

[0002]

[Description of the Prior Art] Generally as for the PDP side of the electromagnetic wave shielding light transmission aperture material arranged in the front face of PDP, the near infrared ray absorption film is stuck. Moreover, a near infrared ray absorption film is stuck for heat ray absorption also on the window glass of an automobile. The alternative absorptivity ability of a near infrared ray is high on the near infrared ray absorption film used for this near infrared ray absorption film, a heat absorbing filter, the filter for video camera visibility amendment, etc., a near infrared ray is intercepted to altitude, and the permeability of a light field is high on it at one side, and it is expected to excel in transparency by colorlessness.

[0003] Conventionally, what formed the near infrared ray absorption layer which distributed the near infrared ray absorbent which consists of a phthalocyanine system, a nickel complex system, an azo compound, a poly methine system, a diphenylmethane system, a triphenylmethane color system, or a quinone system compound on the transparency base material film front face into the base polymer as a near infrared ray absorption film is offered. Moreover, in order to raise near infrared ray absorption efficiency and light permeability, the near infrared ray absorption film which made two or more sorts in these near infrared ray absorbents contain in a near infrared ray absorption layer is proposed by JP, 11-95026, A.

[0004]

[Problem(s) to be Solved by the Invention] If it is in a near infrared ray absorption film, to excel in thermal resistance, moisture resistance, ultraviolet resistance, etc. is further demanded on the operating environment. Especially with the near infrared ray absorption film arranged in the front face of PDP, since it is exposed to a long duration high temperature service by generation of heat from PDP, to excel in thermal resistance is demanded. Moreover, thermal resistance is required also about the near infrared ray absorption film stuck on the window glass of an automobile.

[0005] However, since the engine performance it may fully be satisfied with the conventional near infrared ray absorption film of the engine performance in thermal resistance etc. is not obtained but near infrared ray absorptivity ability falls by use by the high temperature service, the improvement is desired. Especially, since the near infrared ray absorption film and PDP of electromagnetic wave shielding light transmission

aperture material approach in connection with the thinning of electromagnetic wave shielding light transmission aperture material in recent years and it is arranged increasingly, if it is in a near infrared ray absorption film, much more heat-resistant improvement is desired.

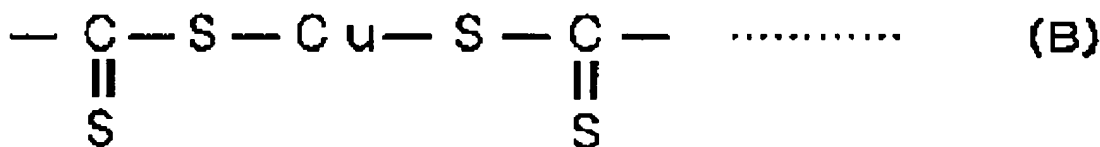
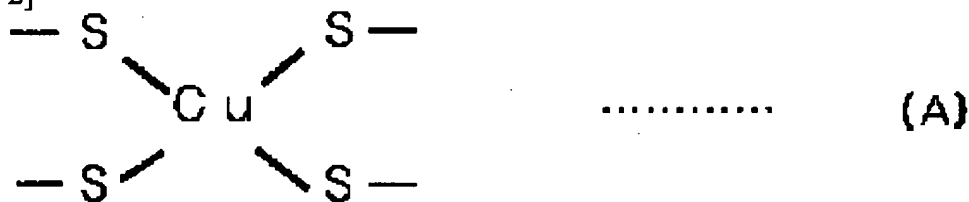
[0006] This invention is made in view of the above-mentioned conventional actual condition, and it excels in heatproof and moisture-proof \*\* ultraviolet resistance, and aims at offering a high endurance near infrared ray absorption film suitable as a near infrared ray absorption film prepared in the window glass of the front face of PDP, or an automobile.

[0007]

[Means for Solving the Problem] The near infrared ray absorption film of this invention is a near infrared ray absorption film characterized by the near infrared ray absorbent which becomes this near infrared ray absorption layer from a G MONIUMU system compound, and the copper compound which has the copper complex and/or the following structure (B) of having the following structure (A) containing in the near infrared ray absorption film with which it comes to form a near infrared ray absorption layer in the front face of a transparence base material film.

[0008]

[Formula 2]



[0009] While using a G MONIUMU system compound according to this invention as a near infrared ray absorbent in a near infrared ray absorption layer, the near infrared ray absorption film which the thermal resistance of a near infrared ray absorption film, moisture resistance, and ultraviolet resistance are improved remarkably, for example, continues also in the use under hot environments at a long period of time, and can maintain near infrared ray absorptivity ability is offered by making the copper complex and/or copper compound of the above-mentioned specification live together as an antioxidant in a near infrared ray absorption layer.

[0010] In this invention, a near infrared ray absorption layer is a layer which distributed the G MONIUMU system compound, the copper complex, and/or the copper compound in the base polymer, and, as for the content rate of the G MONIUMU system compound

in this near infrared ray absorption layer, it is desirable that the content rate of the 0.01 - 100 weight section, a copper complex, and/or a copper compound is the 0.01 - 100 weight section to the G MONIUMU system compound 100 weight section to the base polymer 100 weight section.

[0011] Moreover, as a base polymer, acrylic resin or polyester resin is desirable, and polyester film is desirable as a transparency base material film.

[0012]

[Embodiment of the Invention] With reference to a drawing, the gestalt of operation of the near infrared ray absorption film of this invention is explained below at a detail.

[0013] Drawing 1 is the sectional view showing the gestalt of operation of the near infrared ray absorption film of this invention.

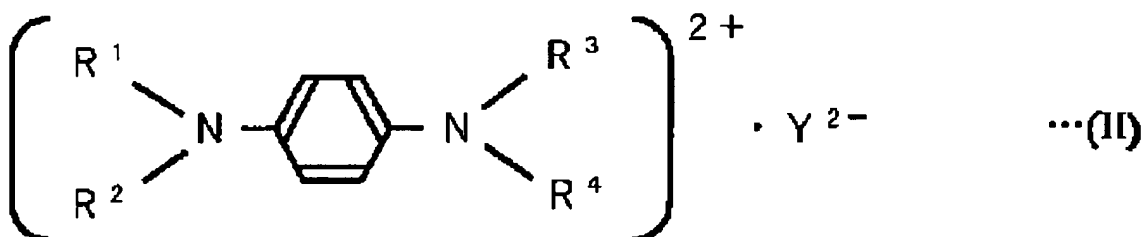
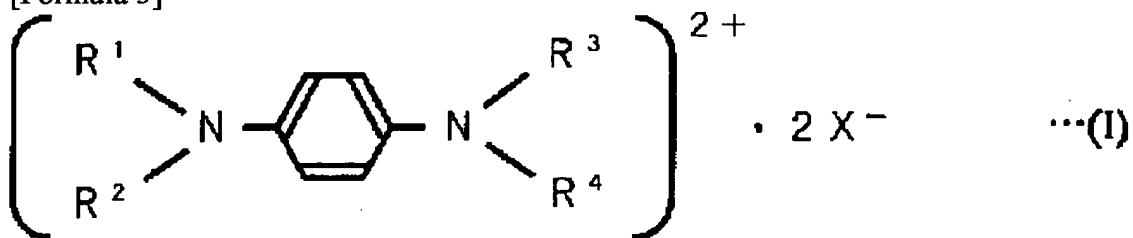
[0014] The near infrared ray absorption layer 3 in which this near infrared ray absorption film 1 contains a G MONIUMU system compound, a specific copper complex, and/or a copper compound on the front face of the transparency base material film 2 is formed.

This near infrared ray absorption layer 3 makes a base polymer distribute a G MONIUMU system compound, a copper complex, and/or a copper compound. The front face of the transparency base material film 1 can be coated with the coating liquid which diluted and carried out concentration adjustment with the suitable solvent, and it can form by drying the coating film.

[0015] this invention -- it is and what is expressed with the following general formula (I) or (II) is mentioned as a G MONIUMU system compound used as a near infrared ray absorbent.

[0016]

[Formula 3]



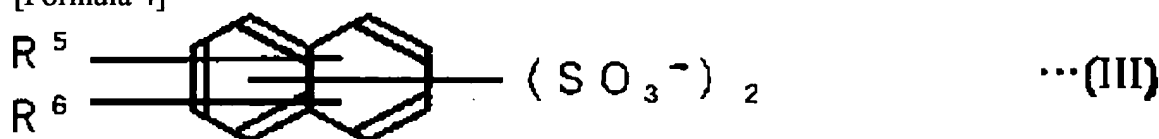
[0017] In addition, R1, R2, R3, and R4 express hydrogen, a halogen atom, an alkyl group, an aryl group, or the functional group of an aromatic series system among the above (I) and the (II) type, and, in X-, a univalent anion and Y2- express a divalent anion.

[0018] As X-, organic sulfonic-acid ion, such as organic carboxylic-acid ion, such as inorganic-acid ion, such as halogen ion, such as I-, Cl-, Br-, and F-, NO3-, BF4-, PF6-, ClO4-, and SbF6-, CH3COO-, CF3COO-, and benzoic-acid ion, CH3SO3-, CF3SO3-, benzenesulfonic acid ion, and naphthalene sulfonic-acid ion, etc. is mentioned. Moreover,

the aromatic series disulfon acid ion which has two sulfonic groups as Y2- is desirable. For example, naphthalene -1, 5-disulfon acid, R acid, G acid, H acid, benzoyl H acid (what benzoyl combined with the amino group of H acid), p-KURORU benzoyl H acid, p-tosyl H acid, Krol H acid (what the amino group of H acid permuted by the chlorine atom), KURORU acetyl H acid, meta-nil g acid, 6-sulfo naphthyl-g acid, C acid, epsilon acid, p-tosyl R acid, naphthalene -1, 6-disulfonic acid, Naphthalene disulfon acid derivatives, such as the 1-naphthol -4 and 8-disulfon acid, Carbonyl J acid, 4, 4'-diaminostilbene -2, a 2'-disulfon acid, Di J acid, naphthalic acid, naphthalene -2, 3-dicarboxylic acid, diphenic acid, A stilbene -4, 4'-dicarboxylic acid, a 6-sulfo-2-oxy--3-naphthoic acid, Anthraquinone -1, 8-disulfon acid, 1, 6-diamino anthraquinone -2, 7-disulfon acid, A 2-(4-sulfophenyl)-6-amino benzotriazol-5-sulfonic acid, 6 -(3-methyl-5-pyrazolo nil)- Ion, such as naphthalene -1, 3-disulfon acid, and a 1-naphthol-6-(4-amino-3-sulfo) ANIRINO-3-sulfonic acid, is mentioned. A more desirable divalent organic anion is naphthalene disulfon acid ion, and the ion expressed with the following general formula (III), for example is mentioned as a still more desirable divalent organic anion.

[0019]

[Formula 4]

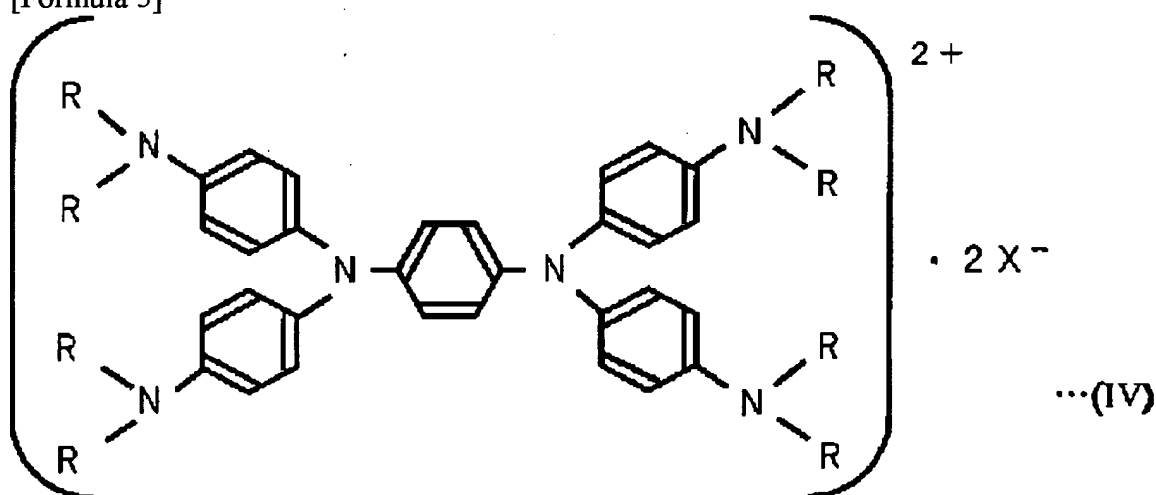


[0020] R5 and R6 express a hydrogen atom, a halogen atom, a low-grade alkyl group, a hydroxyl group, an alkylamino radical, the amino group, -NHCOR7, -NHCO two R7, -OSO two R7 (it is here and R7 expresses the alkyl group which is not permuted [ the aryl group which is not permuted / a permutation or /, a permutation, or ]), or an acetyl group among the above-mentioned (III) formula.

[0021] As a suitable thing of such a G MONIUMU system compound, what is expressed with the following general formula (IV) is mentioned.

[0022]

[Formula 5]



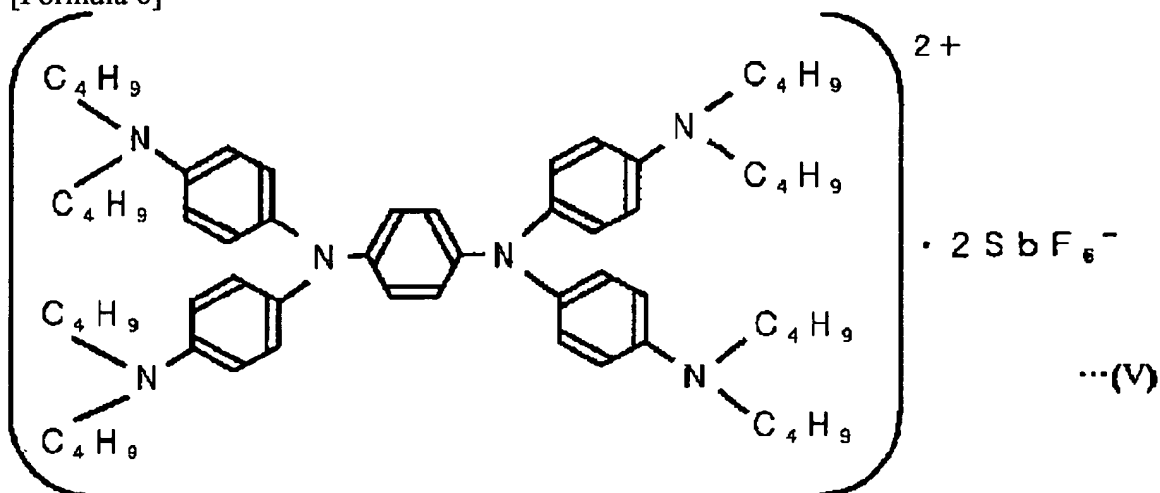
[0023] the inside of the above-mentioned (IV) type, and R -- the alkyl group of carbon numbers 1-8 -- it is n-butyl preferably and BF4-, PF6-, ClO4-, and SbF6- are mentioned

preferably as X-.

[0024] As a concrete G MONIUMU system compound, what is expressed with the following structure expression (V) is mentioned.

[0025]

[Formula 6]

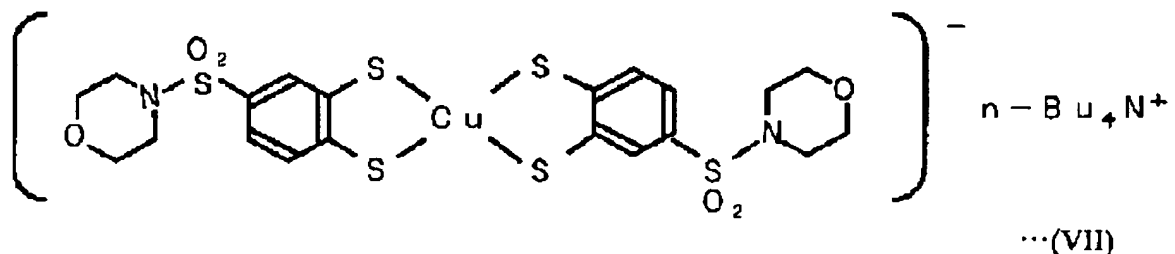
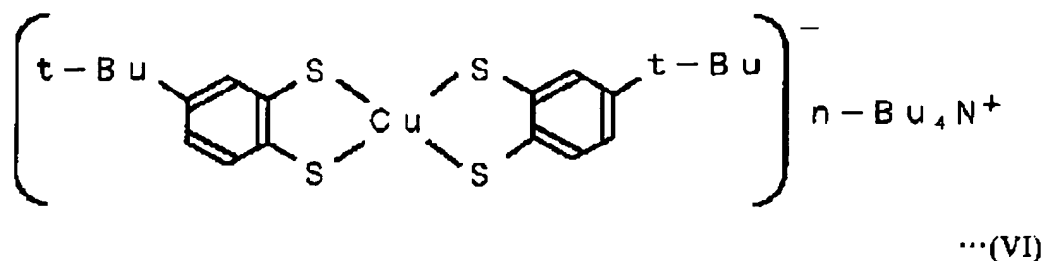


[0026] Moreover, as a copper complex which has said structure (A), 1 and 2-benzenethiol copper complex system compound is mentioned, and 4-morpholino sulfonyl -1 expressed with the screw (4-t-butyl -1, 2-dithio phenolate) copper-tetra--n-butyl ammonium specifically expressed with the following structure expression (VI) or the following structure expression (VII) and 2-benzene dithiol copper complex are mentioned.

[0027]

[Formula 7]



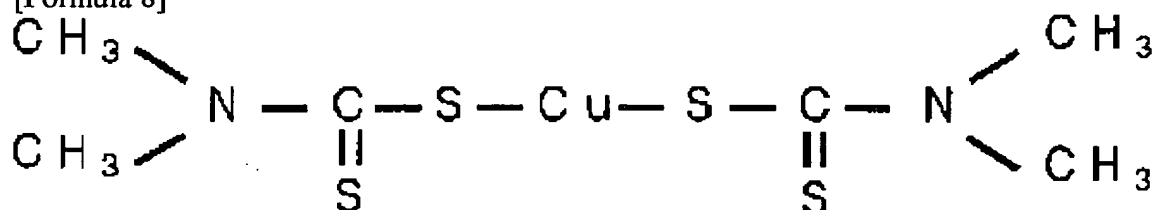


(Bu : ブチル基)

[0028] Moreover, as a copper compound which has said structure (B), the dimethyl dithiocarbamic acid copper expressed with the following structure expression (VIII) is mentioned.

[0029]

[Formula 8]



[0030] A commercial item can be suitably used for each of these G MONIUMU system compounds and copper complexes, and/or copper compounds.

[0031] In this invention, if many [ if there are too few contents of the G MONIUMU system compound in a near infrared ray absorption layer, they run short of near infrared ray absorption effects, and / too ], since light permeability will worsen, it is desirable the 0.001 - 100 weight section especially 0.01 - 50 weight section, and to especially make a G MONIUMU system compound into 0.1 - 10 weight section to the base polymer 100 weight section.

[0032] Moreover, since they run short of the improvement effectiveness in endurance, such as thermal resistance and moisture resistance, if there are too few the copper complexes and/or copper compounds in a near infrared ray absorption layer, a near infrared ray absorption layer will color if many [ too ], and the appearance of a near infrared ray absorption film worsens, it is desirable the 0.01 - 100 weight section

especially 0.1 - 50 weight section, and to especially make a copper complex and/or a copper compound into 0.5 - 30 weight section to the G MONIUMU system compound 100 weight section.

[0033] In addition, as a base polymer of a near infrared ray absorption layer, acrylic resin or polyester resin is preferably used for a homopolymer or a copolymer of polyester resin, acrylic resin, methacrylic resin, urethane resin, silicone resin, phenol resin, and acrylic ester (meta) etc.

[0034] On the other hand, especially as a transparency base material film, although not limited, a polyester system, acrylic, a cellulose system, a polyethylene system, a polypropylene system, a polyolefine system, a polyvinyl chloride system, a polycarbonate system, a phenol system, an urethane system resin film, etc. are used, and a polyester system resin film is especially used preferably from viewpoints, such as transparency and a resistance to environment.

[0035] As a transparency base material film, it is desirable to use the thing of 10 micrometers - about 1mm of thickness from the field of a mechanical strength and thinning.

[0036] Moreover, as for a near infrared ray absorption layer, it is desirable to be formed in about 0.5-50 micrometers in thickness from the field of near infrared ray absorptivity and light permeability.

[0037] In addition, it sets in the range which spoils neither the near infrared ray absorptivity ability, nor light permeability, endurance, etc. in a near infrared ray absorption layer. Additives other than said copper complex and/or a copper compound may be blended with a G MONIUMU system compound list. On near infrared ray absorbents other than a G MONIUMU system compound, and a concrete target, for example, a phthalocyanine system, A nickel complex system, an azo system, a poly methine system, a diphenylmethane system, a triphenylmethane color system, Near infrared ray absorbents, such as a quinone system, and said copper complex and/or antioxidants other than a copper compound, The antioxidant of a phenol system, an amine system, a hindered phenol system, a hindered amine system, a sulfur system, a phosphoric-acid system, a phosphorous acid system, and a metal complex system may specifically be blended, and an ultraviolet ray absorbent may be blended from a viewpoint of the improvement in endurance to ultraviolet rays. Furthermore, the coloring agent for amelioration of the appearance of a film, a pigment, coloring matter, etc. may be blended.

[0038]

[Example] An example and the example of a comparison are given to below, and this invention is more concretely explained to it.

[0039] The near infrared ray absorption stratification ingredient of combination shown in examples 1-8, the example 1 of a comparison, and two table 1 was dissolved in the partially aromatic solvent (dichloromethane 18.5g, tetrahydrofuran 37g, and toluene 37g), coating liquid was prepared, the polyethylene film with a width of face [ of 200mm ] and a thickness of 100 micrometers was coated with this coating liquid, it dried at the room temperature, and the near infrared ray absorption layer with a thickness of 5 micrometers was formed.

[0040] This near infrared ray absorption film was held at 80 degrees C for 500 hours, from the absorbance of order, 1090nm absorbance survival rate was computed by the

following formula, and the result was shown in Table 1.

[0041]

[Equation 1]

$$1090\text{nm吸光度残存率} = \frac{80^{\circ}\text{C}, 500\text{時間経過後の}1090\text{nm吸光度}}{\text{初期}1090\text{nm吸光度}}$$

[0042]

[Table 1]

例	実施例								比較例	
	1	2	3	4	5	6	7	8	1	2
近赤外線吸収層形成材料 (g)										
ベースポリマー ※1	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
ジイモニウム系化合物A ※2	0.25	0.25	0.22	0.3	0.35	—	—	—	0.28	0.32
ジイモニウム系化合物B ※3	—	—	—	—	—	0.25	—	—	—	—
ジイモニウム系化合物C ※4	—	—	—	—	—	—	0.25	—	—	—
ジイモニウム系化合物D ※5	—	—	—	—	—	—	—	0.25	—	—
銅ジチオレン系錯体A ※6	0.025	—	—	—	—	—	—	—	—	—
銅ジチオレン系錯体B ※7	—	0.025	0.006	0.1	0.035	0.025	0.025	0.025	—	—
Niジチオレン化合物 ※8	—	—	—	—	0.28	—	—	—	—	0.28
1090nm吸光度残存率	0.94	0.94	0.92	0.92	0.84	0.90	0.91	0.92	0.78	0.71

※1: 旭化成工業社製ポリエステル樹脂「デルベツト80N」

※2: 日本カーリット社製「CIR-1081」化合物名はN, N, N', N'-テトラキス(p-ジブチルアミノフェニル)-p-フェニレンジイモニウムの六フッ化アンチモン酸塩

※3: 日本カーリット社製「CIR-1080」化合物名はN, N, N', N'-テトラキス(p-ジブチルアミノフェニル)-p-フェニレンジイモニウムの過塩素酸塩

※4: 日本カーリット社製「CIR-1083」化合物名はN, N, N', N'-テトラキス(p-ジブチルアミノフェニル)-p-フェニレンジイモニウムのテトラフルオロリン酸塩

※5: 日本化薬社製「IRG-022」化合物名はN, N, N', N'-テトラキス(p-ジブチルアミノフェニル)-p-フェニレンジイモニウムの六フッ化アンチモン酸塩

※6: 住友精化社製「BBT」化合物名はビス(4-tert-ブチル-1, 2-ジチオフェノール)銅-テトラ-tert-ブチルアンモニウム

※7: 住友精化社製「EST」化合物名は4-モルホリノスルホニル-1, 2-ベンゼンジチオール銅錯体

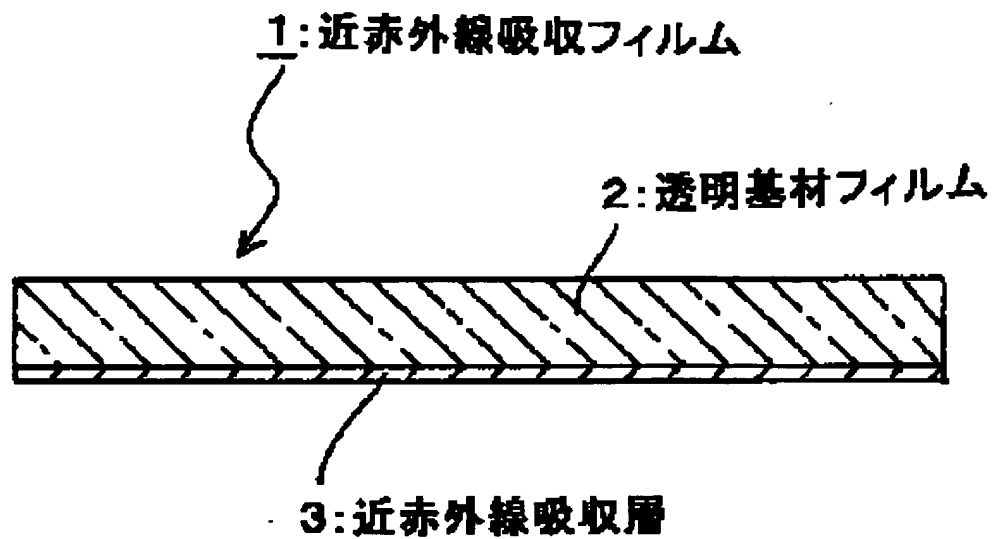
※8: みどり化学社製「MIR-101」化合物名はビスジチオベンジルニッケル

[0043] If it is the near infrared ray absorption film of this invention which blended the G MONIUMU system compound and the copper JICHIOREN system complex with the near infrared ray absorption layer so that more clearly than Table 1, even after holding at 85 degrees C for 500 hours, it turns out that 0.8 or more good results are obtained and 1090nm absorbance survival rate is excellent in thermal resistance.

[0044]

[Effect of the Invention] According to this invention, it excels in thermal resistance, moisture resistance, ultraviolet resistance, etc. remarkably, and the near infrared ray absorption film of high endurance which continues at a long period of time and does not have the problem of a fall of near infrared ray absorbing power is offered as explained in full detail above.

[0045] Such a near infrared ray absorption film especially of this invention is suitable as a near infrared ray absorption film arranged in the front face of PDP exposed to the bottom of long duration and a high temperature environment.



---

[Translation done.]